Synthetic Organic Chemicals

PUBLISHED BY THE
EASTMAN KODAK COMPANY, ROCHESTER, NEW YORK

VOL. VII JULY, 1934 No. 5

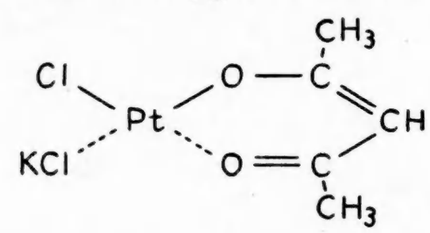
Chelate Compounds

THE term "Chelate" (from χηλή, the crab's claw) was given by Morgan and Drew (J.C.S. *117*, 1457, 1920) to a class of compounds possessing some very unusual properties. The true nature of these compounds was for a long time unknown. Light was cast upon them by the introduction of Werner's theory of residual valence and, in recent years, by the increased knowledge of atomic linkages: namely, the electrovalent, the covalent, and the special application of the latter, the co-ordinate link.

Perhaps the most remarkable of this type of compounds are the metallic derivatives of β-diketones and particularly of acetyl acetone $(CH_3.\underset{\underset{O}{\|}}{C}.CH_2.\underset{\underset{O}{\|}}{C}.CH_3)$.

In the latter part of the 19th century, Combes (Compt. rend. *119*, 1221, 1894) prepared a series of metallic derivatives of acetyl acetone and found them to possess properties differing from those possessed by normal metallic salts. They are difficultly soluble in water, in which they are neither conducting nor hydrolyzed, but are easily soluble in organic solvents such as benzene or chloroform. Unlike most salts, these compounds have low melting points and are volatile, often at atmospheric pressure, without decomposition. Since the work of Combes, over 60 derivatives of acetyl acetone of the type NaA, BeA_2, AlA_3, and ZrA_4 have been prepared which originally were assumed to be salts because of the ease with which the molecule could be represented as an open chain. A few, such as those of the alkali metals, have proved to be salts, but the vast majority have the above-mentioned properties which remove them from the salt category.

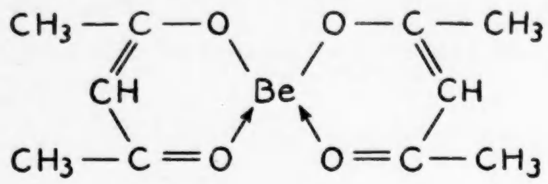
In 1901, Werner (B. *34*, 2584, 1901), while working with the platinum derivatives of acetyl acetone, postulated the possible existence of a link, due to residual valence, between the platinum and the second oxygen atom thus:



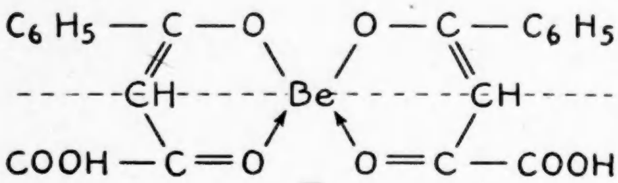
In 1907, Tschugaeff (J. Pr. Chem. *75*, 153) suggested the possibility of the formation of rings by means of co-ordinate links in biuret and similar compounds; and, in 1908, Werner (B. *41*, 1062, 1908) further developed the idea to include a large number of compounds including such metallic derivatives of β-diketones as acetyl acetone, and, on the other hand, compounds formed by dyes with mordants.

With the advent of the present theory of the shared electron, the structure of chelate compounds has been further advanced. It is now thought that a co-ordinate bond is established between

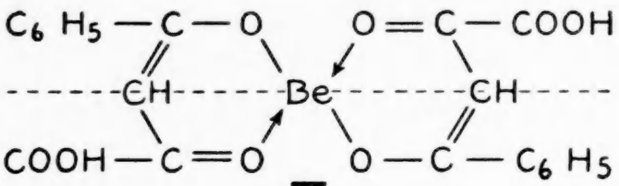
the metal atom and the second oxygen of the diketone, the oxygen being the donor and the metal, the receiver, thus forming a more or less rigid ring. Beryllium acetyl acetone, for example, would then be written thus:



This ring structure has been further substantiated by the work of Mills and Gotts (J.C.S. 3121, 1926) who succeeded in resolving the beryllium derivative of benzoyl pyruvic acid into its two optical isomers, I and II.



I



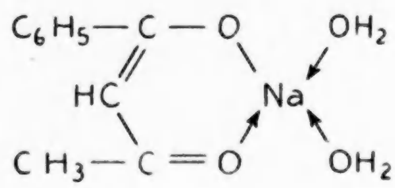
II

The formation of chelate compounds is not limited to derivatives of β-diketones only. Certain diamines, β-ketonic esters, o-hydroxy aromatic esters and aldehydes, and o-nitro phenols are some compounds that also exhibit this property. Sidgwick and coworkers (J.C.S. *125*, 527, 1924; *127*, 907, 1925) have proved, by means of solubility data, that free ortho substituted phenols (particularly nitro and aldehydo), and the enolic forms of β-diketones and β-ketonic esters exist as chelate rings in which the hydroxyl takes part.

I

II

Another curious phenomenon has been noticed in the case of the alkali derivatives of certain compounds. The anhydrous forms, by their insolubility in organic solvents and solubility in water, definitely show themselves to be salts. However, the same salts, when hydrated, lose their water solubility and acquire a solubility in organic solvents indicating the presence of a co-ordinate link. Sidgwick and Brewer (J.C.S. 2379, 1925) explain this by the assumption of the formation of a chelate ring as follows:



Alkali derivatives may be divided into three classes. Those of Class I are always salts; those of Class II are chelate when first produced but on separation change to a more stable ionized form; and those of Class III are stable in the non-polar form. As a rule, lithium derivatives are always salts, and sodium and potassium derivatives vary. If the sodium derivative falls in Class II, the potassium will usually be in Class I. (Sidgwick and Brewer, J.C.S. *127*, 2379, 1925.)

Chelate compounds may be classified in two ways—either by the nature of the links which hold the ring together or by the number of atoms which the ring contains. Under the former system, there are three types: Type A, wherein the ring is formed by two normal valences; Type B, by one normal and one co-ordinate valence; and Type C, by two co-ordinate valences. Under the latter system, rings consisting of four to eight members are known.

A valuable and interesting source of information as to the nature of chelate rings lies in a study of the structure of mordant dyes. Conversely, it is true that the phenomenon of mordant dyeing may be better understood through a

knowledge of chelate compounds. For example, in the 1914 edition of Schultz's Farbstofftabellen, there are some 160 dyes of established constitution that can be mordanted with polyvalent metals. Of these, all but a half dozen contain a replaceable hydrogen atom and a donor atom so disposed as to be capable of forming a five- or six-membered ring attached to the aromatic ring in the ortho position. (Sidgwick Electronic Theory of Valence, p. 234.)

The Sugar Acids

Characteristic of sugars is their ability to yield acids upon suitable oxidation. Acids, thus derived, form a group of organic compounds which are referred to as the "sugar acids," and whose nomenclature has been carried over from the parent sugars.

These acids may be divided into four major types:

I. The -onic acids, originating by the oxidation of the aldehydic group to a carboxyl.

II. The -uronic acids, obtained by the oxidation of the primary alcoholic group to a carboxyl after protecting the aldehydic group.

III. The dicarboxylic acids, obtained by complete oxidation of both the aldehyde and the primary alcoholic groups to carboxyls.

IV. The keto -onic acid, obtained by the oxidation of the 1 and 2 carbons to the carboxyl and carbonyl, respectively.

This latter type of acid (No. IV) is particularly interesting in that it may be further oxidized to yield the -onic acid corresponding to the sugar of one carbon less than the original keto -onic acid. Thus, for example, glucose may yield gluconic, glucuronic, saccharic, keto-gluconic, or arabonic acids, depending upon the type and severity of oxidation. As a rule aldoses are more amenable to oxidation than are ketoses, since the latter are very susceptible to splitting of the carbon chain.

Sugars may be oxidized in acid, alkaline or neutral solution, the choice depending upon the ease of oxidation and the desired product.

Acid oxidants, such as chlorine, bromine, and dilute nitric acid yield -onic acids, most generally as the corresponding lactones. Concentrated nitric acid yields a dicarboxylic acid. With the latter reagent, ketoses split between the α and β carbons to yield formic acid and a dicarboxylic acid.

Alkaline oxidation may be brought about by such reagents as metal oxides, bromine, and hydrogen peroxide. This has a decided disadvantage as it is difficult to control and yields a variety of products due to splitting of the carbon chain.

Among the neutral oxidants may be mentioned hydrogen peroxide. This reagent is claimed to yield some glucuronic acid directly from glucose. However, it tends to cause splitting, for acids of fewer carbons are also found.

Latest evidence concerning the mechanism of oxidation of sugars indicates that, after oxidation in the presence of barium carbonate with bromine water, the lactone is the primary product which then reacts with water to form the corresponding acid. This conclusion is based upon the fact that the primary products of oxidation are not acidic but develop acidity in aqueous solutions on standing. The lactone has been experimentally shown not to be acidic.

These results permit the conclusion that there is no disruption of the sugar ring during oxidation. Conversely, they lend further support to the 1,5 ring structure of normal sugars, for such sugars as *d*-mannose and *l*-rhamnose yield, after oxidation by the above described method, the delta lactones.

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Eastman Organic Chemicals as Analytical Reagents

XXXIII REAGENTS FOR BISMUTH

FORMALDEHYDE

Rupp and Hamann, ZEIT. FÜR ANAL. CHEM. *87*, 32 (1931)

Bismuth is precipitated as the metal by treating a solution containing a little glycerol and not more than 0.3 gm. bismuth with a formaldehyde solution and an excess of sodium hydroxide. The solution is warmed on the water bath and then heated with more formaldehyde. The precipitate is filtered through an Allihn tube, washed with water, alcohol, and ether, and then dried by passing dry hydrogen through the heated tube.

8-HYDROXYQUINOLINE

Sazerac and Pouzergues, COMPT. R.S. BIOL. *109*, 370 (1932)

Bismuth salts form with this reagent a red-orange or red-violet compound which is soluble in a mixture of 2 parts of acetone and 1 part of amyl acetate. Two cc. of the bismuth solution are shaken with 0.2 cc. of reagent and 1.5 cc. of mixed solvent. By comparison of colors the bismuth can be accurately determined in amounts between 2 and 100 mg.

QUINOLINE

Korenman, PHARM. ZENTR. *71*, 769 (1930)

Salts of bismuth and a number of other metals form crystalline compounds with quinoline. These compounds can be used to identify the metals by microscopic examination.

THIOUREA

Mahr, ZEIT. FÜR ANAL. CHEM. *94*, 161 (1933)

The yellow color produced by thiourea with solutions of bismuth is made the basis of a colorimetric method. The sample is heated with nitric acid, and the solution finally adjusted to a concentration of 4½-5½% HNO_3. The addition of solid thiourea precipitates most of the foreign metals which are filtered off and washed with a thiourea solution. The combined yellow filtrates are diluted to a definite volume and matched against known standards of bismuth nitrate treated similarly. With samples as small as 0.5 gm., it was found possible to detect with accuracy amounts of bismuth as low as 0.01%.

New Eastman Organic Chemicals

T 3677	Aminoazobenzenesulfonic Acid (Technical)	1 kg.	$2.80 E
P 3616	5-Chloro-2-aminotoluene (Practical) MP 14-18°	1 kg.	7.00 E
3641	Decamethylene Glycol MP 70-73°	10 g.	2.00 A
3630	4,4′-Tetramethyldiamino-4″-methoxytriphenylmethane MP 105-106°	100 g.	6.00 C
3628	4,4′-Tetramethyldiamino-4″-methyltriphenylmethane MP 94-95°	100 g.	6.00 C
3660	4,4′-Tetramethyldiamino-3″-nitrotriphenylmethane MP 152-153°	100 g.	6.00 C
3650	4,4′-Tetramethyldiamino-4″-hydroxytriphenylmethane MP 161-163°	100 g.	6.00 C
3651	4,4′,4″-Hexamethyltriaminotriphenylmethane MP 178-179°	100 g.	6.00 C
3620	4,4′-Tetramethyldiaminotriphenylmethane MP 102-103°	100 g.	6.00 C